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CHEMICAL CORPS MEDICAL LABORATORIES
RESEARCH REPORT

MLRR No. 379

REACTION OF SARIN WITH BLEACH IN DILUTE AQUEOUS SOLUTION (U)

by

Joseph Epstein
Virginia E. Bauer
Mary M. Demek

July 1955

ARMY CHEMICAL CENTER, MARYLAND

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ABSTRACT

Sarin is rapidly hydrolyzed in mildly alkaline waters (pH = 7.0-9.0) containing comparatively low concentrations of high test bleach (HTH) or sodium hypochlorite solutions. Chloramine T does not accelerate the hydrolysis rate of Sarin to an appreciable extent. The rate of the reaction is proportional to the first powers of Sarin and hypochlorite ion concentration. An approximate bimolecular rate constant for the reaction at 25° C. is 560 $l.mole^{-1} min.^{-1}$, and the change in rate for each 10° C. change in temperature is approximately two. Because the rate is dependent upon the hypochlorite ion concentration, it is also dependent within limits, upon pH, since hypochlorous acid has a dissociation constant of about 4×10^{-8}. To show this more clearly, the half life of Sarin in minutes at different temperatures and values and with different concentrations of chlorine is as follows:

$T^{\circ}C$	pH	Conc. Cl_2 ppm	$t\frac{1}{2}$ Min.
25	6.0	200	11
	7.0	25	13
2-3°	6.0	200	38
	7.0	100	12
	8.0	100	3
	9.0	50	4

This finding, it is believed, is important because it makes possible a water treatment by a single procedure which can be effective against many CW and BW materials.

Medical Laboratories Research Report No. 379

Reaction of Sarin with Bleach in Dilute Aqueous Solution

I.   INTRODUCTION.

A. Object.

The object of this work was to study the reaction between dilute solutions of Sarin and active chlorine compounds.

B. Authority.

Authorized by Chief Chemical Officer under Projects 4-08-03-014, Evaluation of CW Water Contaminants and 4-08-06-002, CW and RW Aspects of Food and Water, Test Program T221, 26 January 1953.

II.   HISTORICAL AND THEORETICAL.

Recent field tests on the decontamination of water containing chemical warfare materials have revealed that, in cold waters, the procedure of raising the pH of the water to a satisfactory operational alkalinity to destroy agents of the G series, particularly Sarin, is not feasible when used with the Corps of Engineers Mobile Purification Unit (1) because of the time required to hydrolyze the agent. During these trials, it was incidentally discovered that relatively high concentrations of chlorine, up to 100 ppm, could be removed almost completely with activated carbon. This suggested that if compounds containing active chlorine were effective decontaminants for the nerve gases, a decontamination procedure might be developed using bleach.

As far as could be ascertained from a literature study, little work has been reported on the reactions of Sarin with active chlorine compounds. Workers at Shell Development Company were unable to evaluate the effectiveness of bleach solutions to decontaminate Sarin due to difficulties in analysis of Sarin after reaction with hypochlorite (9). A study made on the release of chlorine in CC_2 (a nitrogen chlorinated material) by Sarin led the investigator to conclude that there is no basis for assuming that CC_2 reacts with Sarin (2).

In our laboratories, it has been established that chloramines such as chloramine T or halazone, in dilute aqueous solution, will not lose their active chlorine when in contact with Sarin, i.e., Sarin does not cause a water to have a "chlorine demand" (6). Furthermore, dogs fed Sarin-contaminated water coagulated with ammonium alum and subsequently treated with bleach to give the solution a 0.5 ppm residual chlorine and pH 6.2 developed symptoms of G agent poisoning (6). On the basis of these two experiments, the conclusion was reached that in very dilute solution, active chlorine compounds do not react, or react only very slowly with Sarin.

In retrospect, however, it should be considered that a "chlorine demand" test gives no information on the state of the Sarin molecule, which is the object of study, for it is evident that an active chlorine compound can conceivably function as a true catalyst, promoting the decomposition of Sarin while remaining unchanged itself. In the experiment in which dogs were used to ascertain the state of the Sarin molecule, the conditions were clouded by the chemicals introduced in the treatment of water.

The present studies show, in fact, that Sarin is rapidly destroyed at neutral or slightly alkaline pH by high test bleach or sodium hypochlorite. The reaction is a catalytic one, and hypochlorite ion is the effective catalyst. The bimolecular rate constant for the reaction at 25° C. is approximately 5.6×10^2 l.mole^{-1} min.$^{-1}$ (using the value of K_A HClO $= 4 \times 10^{-8}$).

Inasmuch as the catalytically active species is the hypochlorite ion and since the hypochlorite ion concentration is markedly dependent upon the pH especially in neutral and slightly alkaline medium, it follows that in neutral or slightly alkaline solutions, the observed velocity of the hypochlorite catalyzed reaction will be pH dependent.*

III. EXPERIMENTAL.

A. Reagents.

1. High Test Hypochlorite (HTH). This material is a product of Mathieson Chemical Corporation. The available chlorine content is 70%. The composition is reported to be as follows:

Calcium hypochlorite	70%
Inert ingredients	30%

A stock solution of HTH was prepared at approximately 4000 ppm Cl_2. The Cl_2 content was determined daily by titration according to well-established procedures. (9a)

2. Sarin - purity > 95%. Solutions of 3 mg./ml. were made up fresh prior to use by diluting weighed quantities of the agent with distilled water.

3. Sodium hypochlorite. This reagent was prepared as follows: Chlorine gas was bubbled slowly into 300 ml. of an ice-cold solution of 1.7 N NaOH solution (prepared by dilution of 50% caustic) until titration of the chlorinated caustic solution showed that the normality of hypochlorite had reached 1.6 N (approximately 80 minutes). Two ml. of

* The hydroxyl ion catalyzed reaction which is also pH dependent is extremely slow as compared to the hypochlorite catalyzed reaction in the pH range under discussion and hence can be neglected.

12.5 N NaOH were then added to raise the pH to approximately 11.0 to insure stability of the solution with respect to active chlorine concentration. A stock solution for the experiments reported herein was made up by diluting 100 ml. of 1.6 N NaOCl and 7.2 ml. of 12.5 N NaOH to 1 liter.

     4.   Chloramine T - USP XII Grade - Mallinckrodt.

     5.   NaOH solutions. Prepared from 50% NaOH solution with carbon dioxide free distilled water and standardized against $KHC_8H_4O_4$. (9c)

     6. $Na_2S_2O_3$ solution. Prepared by dissolving 25 g. $Na_2S_2O_3 5H_2O$ (C.P.) in distilled water containing 2 g. Na_2CO_3 and diluting to 2 liters. Standardized against potassium biiodate (9b).

     7.   Schoenemann Test Reagents.

     a.   Peroxide - Calgon mixture - aqueous solution, 5.0% with respect to calgon and 0.4% with respect to H_2O_2.

     b.   Buffer - indicator mixture. The mixture was composed of 200 ml. of 0.05 M phosphate buffer (pH = 8.7), 200 ml. C.P. acetone, 100 ml. 1.0% aqueous o-tolidine dihydrochloride, and sufficient distilled water to make up 500 ml.

     c.   Perdox reagent - 1.0% Perdox (low alkalinity) aqueous solution. The solution was made up fresh daily. Perdox is a commercial brand of sodium perborate.

    B.   Equipment.

     1.   Beckman pH meter - Model G - standardized daily with pH 7.0 buffer; checked at pH 4.0 and 8.0 (Fisher Scientific Company reagents).

     2.   Assorted laboratory glassware.

     3.   Thermometer, 0° - 100° C.

     4.   Klett-Summerson Photoelectric colorimeter with 420 mμ filter.

     5.   Precision Scientific Company, Mag-Mix Magnetic Stirrer and Teflon covered Magnetic-Stirring Bar.

    C.   Analytical Methods.

     1.   Determination of Sarin.

     The experience gained in the study of the mechanism of the reaction involving Sarin and the dye precursor tetramethyldiaminophenyl

(4,5-dimethyl-2-thienyl) methane was helpful in devising a procedure for the estimation of G agents in the presence of hypochlorite ion (7). The procedure used was an adaptation of the familiar Schoenemann Test except that hydrogen peroxide solution was added to destroy the active chlorine prior to the addition of other reagents. For concentrations of Sarin above 10 ppm the procedure was as follows:

To 10 ml. of the sample to be analyzed in a 100 ml. volumetric flask was added 2 ml. of the calgon-hydrogen peroxide mixture. The solutions were mixed well and within 30 seconds 10 ml. of the buffer-indicator mixture were added followed by 4 ml. of the perdox reagent. The solutions were mixed well, diluted to volume and read after 30 minutes in a Klett-Summerson colorimeter using a 420 mµ filter. With solutions containing approximately 10 ppm of Sarin, 20 ml. aliquots of the Sarin-hypochlorite solutions were used. For the highest concentration of active chlorine used in these tests, viz, 200 ppm, it was necessary to add 2 ml. of 0.4% hydrogen peroxide solution to the aliquot in addition to the 2 ml. of the calgon-hydrogen peroxide reagent to effectively destroy all the active chlorine compound.

A standard curve was constructed using solutions of known Sarin concentration (Figure 1). It was demonstrated that hypochlorite did not interfere in this determination by comparing standard curves of solutions containing Sarin to which had been added hypochlorite and hydrogen peroxide in rapid succession, with those obtained using Sarin only. The curves prepared in both ways were, within experimental error, identical (See Figure 1)*.

2. Hypochlorite Concentration.

To an aliquot of hypochlorite solution was added 5 potassium iodide pellets (1.6 g) and 5 ml. of 12.0 N HCl. The iodine was titrated with 0.05068 N $Na_2S_2O_3$ solution to the disappearance of the starch-iodine color.

3. Calculation of Results.

It was established that the action of hypochlorite ion on Sarin is catalytic (see footnote to Table I and discussion). A discussion of the measurement of the rate of disappearance of Sarin by acid formation and by Sarin analysis in catalytic reactions is given in a previous

* A further check on the adequacy of this method was made by correlation of oral toxicity determinations with the intensity of color (concentration) produced by reacting solutions containing Sarin and hypochlorite according to the method described above. It was found that when a Sarin-hypochlorite mixture after standing produced a color in the modified Schoenemann test whose intensity indicated that only one-tenth of the original concentration remained, approximately ten times the volume of the aged solution was required to produce the same effect as the original solution by oral administration.

publication (5). Adjustments were made in the calculations of the concentrations of Sarin by acid production to compensate for the changes in volume of reaction solution caused by removal of aliquots for the test by the o-tolidine perborate method. The first order rate constants were calculated from the equation -

$$K_{obs} = \frac{.693}{t\frac{1}{2}} = K_1 + K_s \tag{a}$$

where $t\frac{1}{2}$ is the time in minutes required for half of the Sarin to disappear, K_{obs} is observed first order rate constant, K_1 is the first order rate constant for the hypochlorite catalyzed decomposition and K_s is the spontaneous hydrolysis rate constant at the pH of the experiment in the absence of hypochlorite. The bimolecular rate constant was calculated from the equation -

$$K_2 = \frac{K_1}{[OCl^-]} \tag{b}$$

where K_2 is in units of $l.mole^{-1}min.^{-1}$ The hypochlorite ion concentration at a given pH was calculated from the pH, the original concentration of the hypochlorite salt and the dissociation constant of hypochlorous acid,

$$[OCl^-] = \frac{K_A C}{H^+ + K_A} \tag{c}$$

where C is the original concentration of hypochlorite salt in mole/l. and K_A is the dissociation constant of hypochlorous acid.

Combining equations (a), (b) and (c) to contain only experimentally measurable quantities, the bimolecular rate constant can be calculated from the equation -

$$K_2 = \frac{[K_{obs} - K_s]}{K_A C} [H^+ + K_A] \tag{d}$$

where K_A is the dissociation constant, chosen for this work as 4×10^{-8}*. The value of K_A is only approximate and hence the absolute value of K_2 will be approximate. The constancy of the K_2 value, which establishes the order of the reaction, will also be dependent upon the value chosen for K_A, but under certain conditions, the importance of K_A can be minimized and for all practical purposes the constancy of the K_2 can be illustrated without an exact value of K_A. Thus if the conditions of the reaction

* The dissociation constant of hypochlorous acid has been the object of study of many workers, with poor agreement among the various investigators. The value of 4×10^{-8} is an average of many individual values reported in the literature.

are such that K_S is small as compared to K_{obs} (which will prevail in slightly acid medium and with a fairly high concentration of the hypochlorite salt), and K_A is small as compared to H^+ concentration, then equation (d) reduces to:

$$K_2 = \frac{K_{obs} \cdot H^+ \cdot}{K_A C'} \tag{e}$$

At two different concentrations of the hypochlorite salt, and two different hydrogen ions concentrations (both large as compared to 4×10^{-8}), since K_2 is a true constant

$$\frac{K_{obs} H^+}{K_A C} = \frac{K_{obs}' H^{+'}}{K_A C'} \tag{f}$$

where K_{obs}', $H^{+'}$, and C' represent an observed velocity constant, hydrogen ion concentration and hypochlorite salt concentration different from that in equation (e). By cancelling the K_A's, it follows that the constancy of the values will depend only upon the observed velocity constant, hydrogen ion concentration and the initial hypochlorite salt concentration.

Except for the K_2 values at pH 8.0 and 9.0, where K_S was either determined or calculated from literature values and subtracted from K_{obs} the values of K_2 were calculated on the assumption that K_S was small as compared to K_{obs} and hence could be neglected.

A K_S value was determined at pH 9.0 to be 1.2×10^{-2} min.$^{-1}$ at 25° C., at pH 8.0, the value of K_S was taken as 1.6×10^{-3} min.$^{-1}$ (3).

The values reported herein are based upon the colorimetric determinations, rather than acid titration. The acid production values served to establish that two moles of acid are produced per mole of Sarin decomposed and as a check on the colorimetric values. All half lives were determined from curves calculated by the method of least squares.

D. Procedure.

Into a 600 ml. beaker containing an accurately measured volume of water was pipetted an aliquot of Sarin solution and a few drops of standard sodium hydroxide solution to adjust the pH to that at which the decomposition was to be measured. An aliquot of accurately standardized hypochlorite solution previously adjusted to the same pH, and of such a volume that the total volume in the beaker would be 500 ml., was then rapidly added. Zero time was taken as the time following addition of one half of the volume of the hypochlorite solution. The reactant solutions were maintained at constant temperature ($\pm$ 0.5° C.) by immersion of the reaction beaker in a water or ice bath. Aliquots of the reaction mixture were extracted and analyzed at various intervals for Sarin content (see

analytical methods). The pH was maintained constant by careful addition of very small volumes of accurately standardized sodium hydroxide solution. The volumes of caustic solution needed to maintain constant pH were recorded at various time intervals.

E. Results.

The results of experiments at approximately 25° C. and at different pH values, using HTH (calcium hypochlorite) are shown in Table I. Typical plots showing the conformity of the decomposition to first order kinetics are shown in Figure 2. Figure 3 shows a plot of the decomposition as determined by both the o-tolidine perborate method (Sarin concentration) and acid production.

Table I

Rate of Decomposition of Sarin (2×10^{-4} M)
at Approximately 25° C. with HTH at Various pHs

pH	Total Hypochlorite Salt Conc. $\times 10^3$	$t\frac{1}{2}$ Min.	$K_{obs} \times 10^2$ Min.$^{-1}$	$K_1 \times 10^2$	$K_2 \times 10^{-2}$ l.mole^{-1}min.$^{-1}$	T °C.
5.0	2.82	96.0	0.72	0.72	6.4	24.5
6.0	.705	42.4	1.63	1.63	6.0	22.0
	2.12	15.1	4.59	4.59	5.6	23.0
	2.82	11.4*	6.08*	6.08*	5.6*	24.5
		11.0*	6.30*	6.30*	5.8*	24.5
7.0	.265	19.2	3.61	3.61	4.8	24.5
	.354	12.7	5.46	5.46	5.4	23.0
8.0	.044	32.7	2.12	2.06	5.9	23.0
	.088	17.4	3.98	2.82	5.4	25.0
	.132	11.6	5.98	5.82	5.3	24.5
	.176	8.3	8.35	8.19	5.6	24.0
9.0	.022	31.0	2.23	1.03	4.8	23.0
	.044	18.8	3.69	2.49	5.8	22.5
	.062	14.5	4.78	3.58	5.9	23.0

* These two runs were made to establish the catalytic nature of the reaction. After the Sarin had been completely decomposed in the first of the two runs ($t\frac{1}{2}$ = 11.4) an additional quantity of Sarin was pipetted into the reaction mixture. The half life of the second quantity of Sarin was 11.0 minutes, demonstrating the existence of the same concentration of the effective catalyst. It might be argued that the concentrations of total hypochlorite salt are quite high as compared to the Sarin concentration, and that if a reaction between 1 mole GB and 1 mole hypochlorite did take place resulting in the decomposition of the hypochlorite, sufficient excess of the hypochlorite salt would remain so that results of the same order as those reported in Table I would be obtained. However, other runs made with concentrations of hypochlorite equal to or less than the concentration of Sarin showed similar behavior. Moreover, the active chlorine titres of the solutions remained unchanged during the course of experiments at pH 7 and 8 where the chlorine concentrations were equal to or less than the Sarin concentrations. For a further discussion on the nature of this reaction see DISCUSSION.

Table II shows the results of experiments run at 2-3° C. at several pH values.

Table II

Rate of Decomposition of 2×10^{-4} M Sarin Solution at 2-3° C. with HTH (calcium hypochlorite) at different pHs

pH	Total Hypochlorite Salt Conc. x 10^3	t½ Min.	K_{obs} x 10^2 Min.$^{-1}$	K_2 x 10^{-2} l.mole^{-1}min.$^{-1}$
6.0	1.41	84.0	0.82	2.0
	2.82	38.1	1.82	2.2
7.0	0.72	21.2	3.26	2.0
	1.41	11.9	5.87	1.9
8.0*	0.72	5.6	12.4	2.3
	1.41	3.0	22.9	2.2
9.0**	0.36	9.8	6.77	2.0
	0.72	4.2	15.8	2.3

* Arbitrarily, a value of $K_A = 3 \times 10^{-8}$ was chosen as the dissociation constant for hypochlorous acid.

** No correction made to K_{obs} since K_s was less than 0.1% of K_{obs}.

At a given temperature, it can be seen that reasonable constancy is obtained (K_2 values) when the hypochlorite ion is considered to be the effective material in the decomposition. An average bimolecular constant at 25° C. is 5.6×10^2 l.mole^{-1}min.$^{-1}$. An approximate bimolecular rate constant at 2-3° C. ($K_A = 3 \times 10^{-8}$) is 2.1×10^2.

The order of the reaction was determined by the differential method described by S. Glasstone, Textbook of Physical Chemistry, 2nd Edition, D. Nostrand Company, 1946, page 1067. The data are shown in Table III.

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Table III

Decomposition Rate of Various Concentrations of Sarin with
Various HTH Concentrations - Temperature = 22-25° C., pH = 6.0

Sarin Conc. $M \times 10^4$	Total Hypochlorite Salt Conc. $M \times 10^3$	$t\frac{1}{2}$ Min.	$K_2 \times 10^2$ Min.$^{-1}$	$K_2 \times 10^2$ l.mole^{-1}min.$^{-1}$
2.14	0.71	42.4	1.63	6.0
2.14	2.12	15.1	4.59	5.6
2.14	2.82	11.4	6.08	5.6
4.28	2.12	17.2	4.03	5.0
8.56	2.12	15.1	4.59	5.6

Analysis of the data shows that the decomposition of Sarin is first order with respect to both the Sarin and the hypochlorite ion concentrations.

One determination at pH 6.0, T = 34° C., showed that the half life of 2×10^{-4} Sarin with 1.42×10^{-3} hypochlorite ion was 12 minutes.

Because of the uncertainty in the values chosen as dissociation constants, the activation energy for this reaction has not been calculated. Instead, a temperature coefficient has been calculated from experimental values at two temperatures, and a calculated value from the third. These data are shown in Table IV.

Table IV

Half Lives of Sarin (2×10^{-4} M) in the presence of 1.42×10^{-3} Hypochlorite Salt (100 ppm Cl_2) at Different Temperatures

Temperature ° C.	$t\frac{1}{2}$	Change in Rate/10° C.
3.5°	84.0	1.82
23.5°	22.6*	
34°	12.0	1.80

*Calculated from $K_2 = 5.6 \times 10^2$; $K_A = 4 \times 10^{-8}$.

Thus, it appears that the decomposition rate is approximately doubled for each 10° C. temperature rise.

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It has been established that at relatively high pH, i.e., 9.0-10.0, calcium and magnesium ions have a catalytic effect on the hydrolysis rate of Sarin (4). The univalent cations sodium and potassium do not exhibit similar behavior.

To determine the effect of the calcium ion in these experiments (and/or the inert ingredients in HTH), two runs were made using sodium hypochlorite, prepared from gaseous chlorine and sodium hydroxide solution.

The half lives of Sarin with two different concentrations of hypochlorite ion supplied by sodium hypochlorite are shown in Table V. For comparison the half life of Sarin with the same concentration of hypochlorite, but supplied by HTH are included.

Table V

Decomposition of 2×10^{-4} M Sarin with Hypochlorite from Sodium Hypochlorite and HTH at pH 6.0; T = approximately 25° C.

Source of Hypochlorite	Total Hypochlorite Salt Conc. M $\times 10^3$	$t_{\frac{1}{2}}$
NaOCl	1.42	19.6
	2.82	11.6
HTH	1.42	22.6*
	2.82	11.4

* Calculated from $K_2 = 5.6 \times 10^2$; $K_A = 4 \times 10^{-8}$

It appears from these results that the rate of decomposition of Sarin in solution of hypochlorite is independent of the nature of the cation, i.e., sodium or calcium, and is dependent only upon the concentration of hypochlorite ion. An experiment was performed to determine the effect of chloramines on rate of decomposition of Sarin. The analytical method reported herein was found to be not as satisfactory in the presence of chloramines as in the presence of hypochlorite. However, by allowing the peroxide to react with chloramine T for a minute and partially diluting the samples before the addition of the buffer-indicator solution, fairly good analytical data were obtained. It was established by acid production and approximate Sarin analysis that the rate of hydrolysis was little or not at all influenced by the presence or absence of chloramine T. It was further established by studying the rate of acid production of a solution containing Sarin, approximately 10 ppm ammonium nitrate and hypochlorite, that the catalytic action of hypochlorite can be completely inhibited by ammonium ions. The inhibition of the hypochlorite is assumed

to be due to the rapid formation of chloramines by the interaction of the ammonium salt with hypochlorite ion. It is known that such a reaction occurs rapidly in dilute solution at neutral pH (10).

IV.   DISCUSSION.

The decomposition of Sarin in aqueous solution by hypochlorite ion offers a possible method for decontamination of water supplies. It is particularly attractive for this use since hypochlorite ion will also destroy many biological materials.

It is important to note the role of pH in this reaction. If HTH is to be used in relatively high concentrations, i.e., 75-200 ppm, there will be, in all probability, no need to adjust the pH of the water since HTH is strongly alkaline itself and will provide the water with alkalinity. If lower concentrations of HTH are to be used, it will be necessary to add a source of alkalinity to the water to maintain a pH (ca. 8) where hypochlorite ion exists in appreciable quantities. Whether the additional alkalinity will be required will depend upon the initial pH of the water, its buffer content and the initial concentration of the agent. (It must be borne in mind that the agent hydrolyzes to form two moles of acid per mole of agent, and in waters of low alkalinity and buffer content can reduce the pH to acid pHs where hypochlorite treatment will be ineffective). However, if gaseous chlorine is to be used, the acidity imparted to the water as a result of the chlorine-water equilibrium may sufficiently lower the pH of the water so as to make the treatment ineffective. It is important also that ammonia or other nitrogen containing compounds be absent. From the experiments on rate of decomposition of Sarin in the presence of chloramine T and the hypochlorite plus ammonium salts, it is evident that hypochlorite ion must be present for effective catalytic action.

It may be that the ineffectiveness of chlorination to destroy the residual Sarin contamination in the experiment referred to in the historical section of this report (6) was due, in part at least, to this phenomenon, since ammonium alum was used prior to chlorination in the coagulation of the water. At the pH of water so treated, viz., 6.2, and the extremely low concentration of active chlorine, a rapid decomposition of Sarin would not be expected, even if hypochlorite ion were present.

Where the time of treatment can be extended to several hours, much lower concentrations of chlorine than those shown in this publication may be used for water decontamination. For example, by maintaining the water at pH 8.0 (which can be easily accomplished with lime or soda ash) addition of only 5 ppm chlorine will reduce the concentration of Sarin in water from 30 to 0.1 ppm in approximately three hours at 25° C.

Nature and Mechanism of the Reaction.

The kinetic studies have shown that the rate of decomposition may be explained by the assumption that the hypochlorite ion is involved. The deduction that the reaction is catalytic follows from the following

observations: First, the rate constants of a double run (see footnote to Table I) were, within experimental error, the same, showing that there had been no decomposition of the material responsible for the acceleration of the destruction of the Sarin. Secondly, the active chlorine titre was unchanged even though the Sarin added had been decomposed. Then, too, two moles of acid are produced per mole of completely decomposed Sarin. Production of the theoretical amount of acid is consistent with a simple hydrolysis and with the absence of side reactions tending to produce more or less acid. Lastly, the decomposition follows first order kinetics. If, in a bimolecular reaction consisting of reactants at approximately equal concentrations, both of the reactants are destroyed, then one would find that a first order plot would not fit the data. Only if one of the reactants remains at constant concentration would first order kinetics be observed.

The rate constant of decomposition of Sarin with hypochlorite is of the same order of magnitude as that found with many reactants (of the same basicity) where reactivity can be explained through a bifunctional attack upon the Sarin molecule, i.e., push-pull mechanism. Work is continuing in an effort to elucidate the mechanism of this reaction. It has already been established that chloride ion is not necessary for the reaction. Studies on the reaction of Sarin with hypochlorous acid in potassium nitrate solution at constant ionic strength show that approximately the same rate constant is obtained with this system as that reported for the sodium and calcium hypochlorite systems (which contained chloride ion due to their methods of preparation) (8).

It does not seem to be too unjustified to compare the structure of the hypochlorite ion with that of the perhydroxyl ion. From Pauling's electronegativity values, it would seem that the oxygen atom would contain a greater share of the electrons shared between the two atoms, and that the chlorine is "electron deficient." The chlorine in hypochlorite ion is generally considered to be positivly charged (electron deficient) and in many of its reactions picks up electrons to form the electronically stable compounds.

An analogous situation probably exists in the perhydroxyl ion, except that the hydrogen of the perhydroxyl group is in the seat of low electron density. An attack upon the phosphorus of the Sarin molecule by hypochlorite ion may be postulated as the initial step in the reaction.

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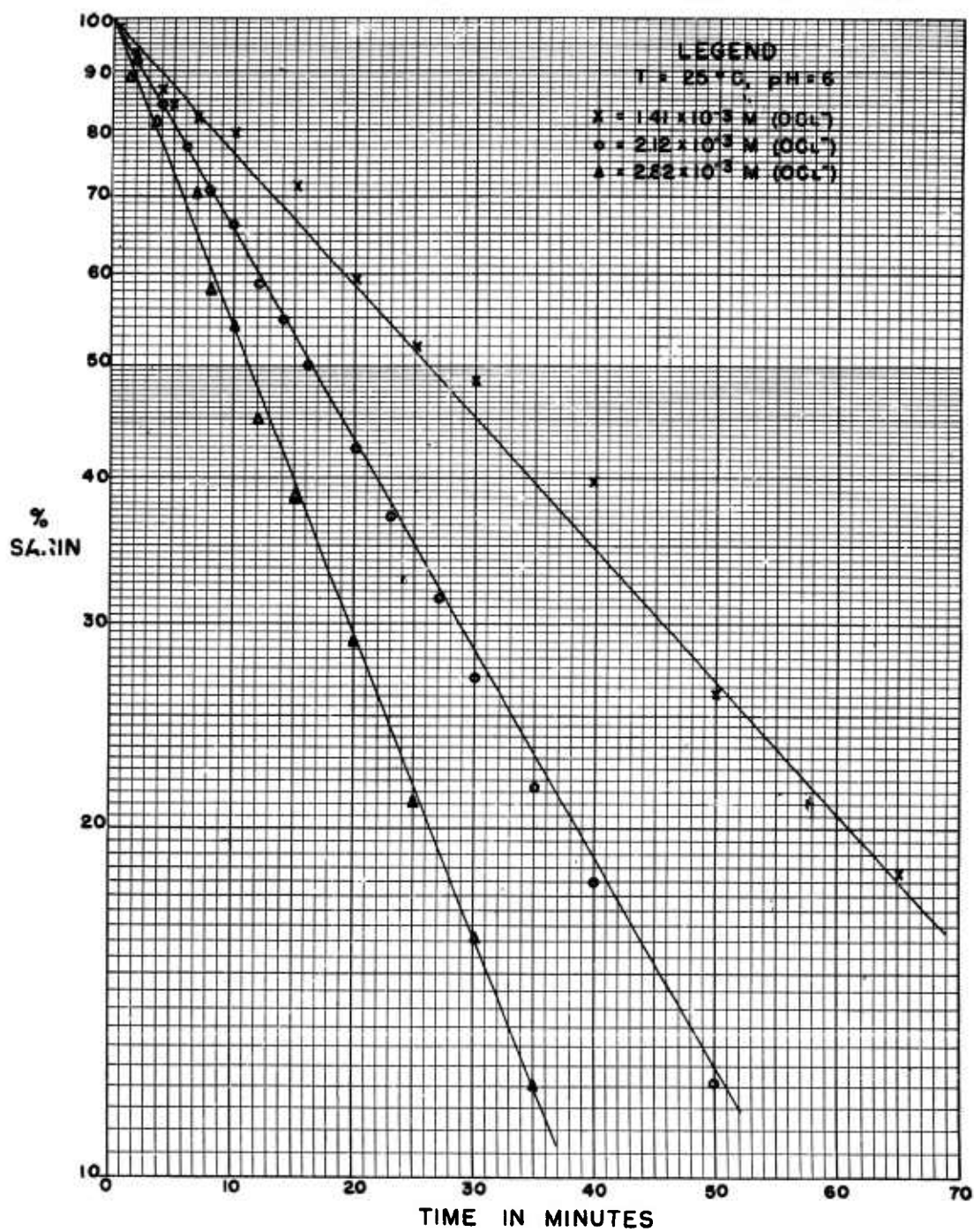FIG. I - EFFECT OF HTH-H_2O_2 TREATMENT ON STANDARDS
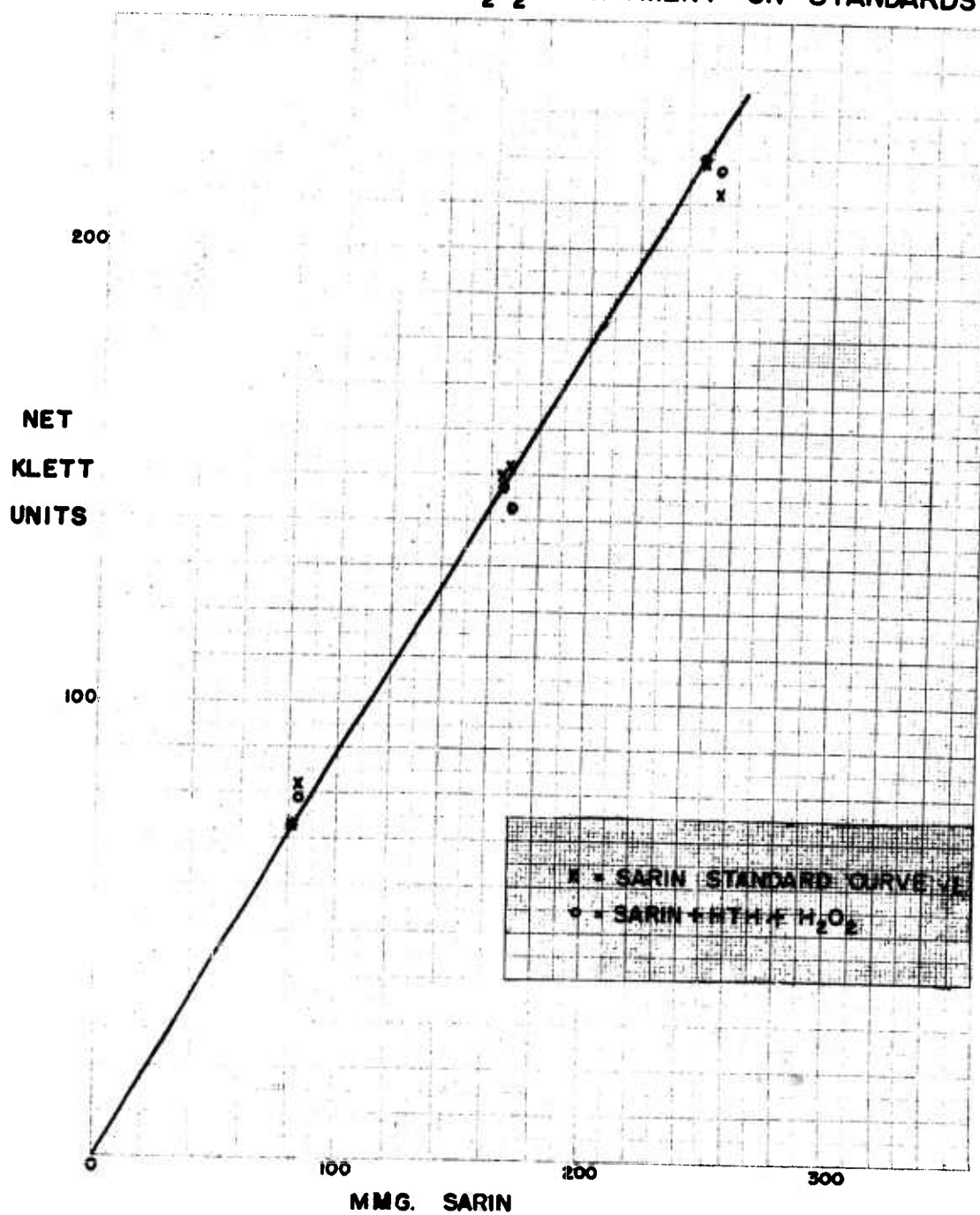
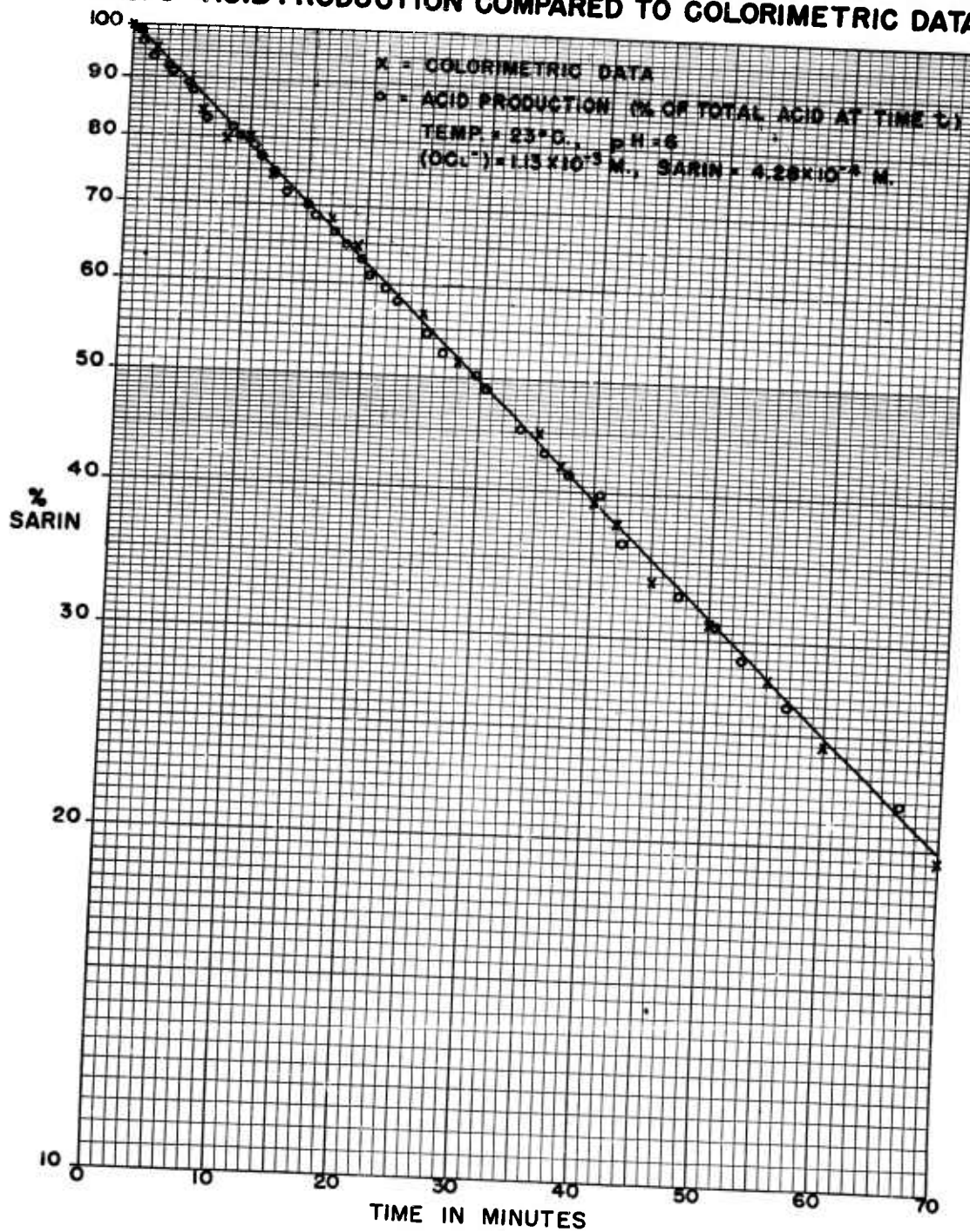# FIG. 2 - EFFECT OF (OCL⁻) ON HYDROLYSIS RATE

LEGEND

T = 25°C, pH = 6

X = 1.41 x 10⁻³ M (OCL⁻)

○ = 2.12 x 10⁻³ M (OCL⁻)

△ = 2.82 x 10⁻³ M (OCL⁻)

%
SARIN

TIME IN MINUTES

FIG. 3 - ACID PRODUCTION COMPARED TO COLORIMETRIC DATA

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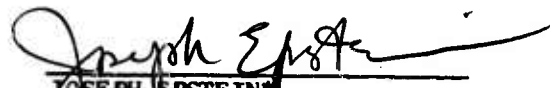
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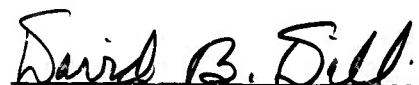
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2. Sarin, chemistry, chloramine T